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Field Investigation of Sulfite Fluxes to a Deciduous Forest

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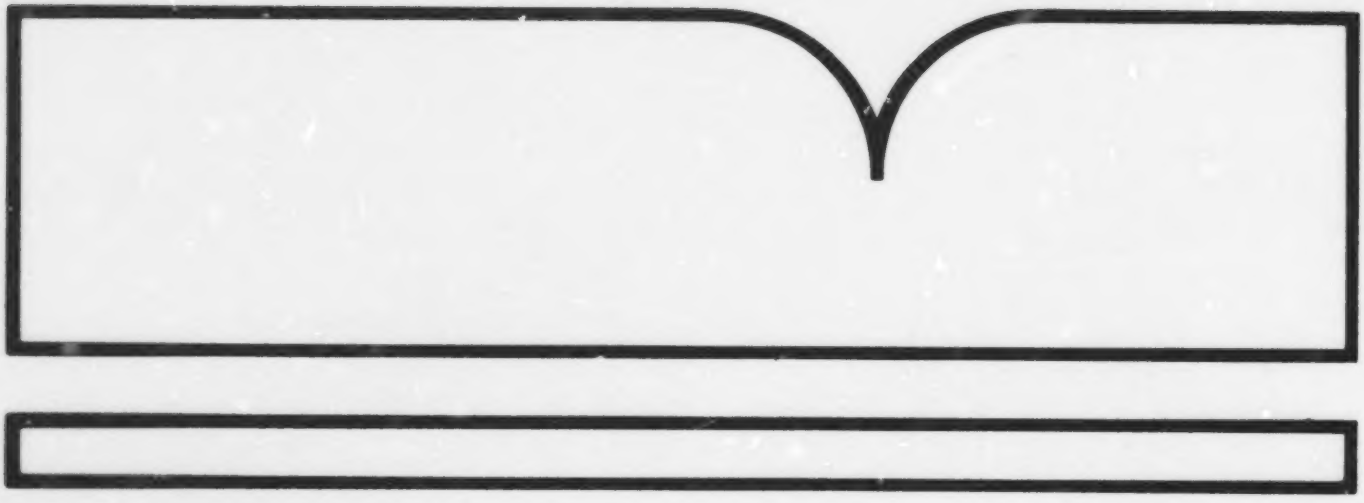

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16. ABSTRACT

An intensive investigation of particulate sulfur fluxes to a deciduous forest was conducted at Oak Ridge, Tennessee, during May 1983. Eddy correlation methods were used to measure fluxes of submicron particulate sulfur, of submicron particles in three different size ranges, and of ozone above the forest canopy. The measured deposition velocities (v_d) of particulate sulfur peaked at about 1 cm s^{-1} in daytime, but dropped to near zero at night, with a long-term average of about 0.6 cm s^{-1}. These values of v_d are consistent with similar measurements taken previously over different surfaces. Measurements and analyses indicate that the flux divergence of particulate sulfur should have caused an error no greater than $\pm$ 0.05 cm s^{-1} in v_d estimates. For very small particles (less than 0.1 μm diameter), measured values of v_d were similar to those for particulate sulfate, but deposition velocities for particles in the accumulation size range decreased as particle size increased, and upward components of fluxes were found in daytime convective conditions.

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A FIELD INVESTIGATION OF SULFATE FLUXES TO A DECIDUOUS FOREST

B. B. Hicks,[1] D. R. Matt,[1] R. T. McMillen,[1] and J. D. Womack[1]
M. L. Wesely,[2] R. L. Hart,[2] and D. R. Cook,[2] S. E. Lindberg,[3]
R. G. de Pena,[4] and D. W. Thomson[4]

Abstract. An intensive investigation of particulate sulfur fluxes to a deciduous forest was conducted at Oak Ridge, Tennessee, during May 1983, as part of a multilaboratory program to study the dry deposition of airborne trace gases and aerosols to vegetated surfaces. At this time, the leaf area was approximately 50% of the maximum and was rapidly increasing. Eddy correlation methods were used to measure fluxes of submicron particulate sulfur (presumably sulfate), of submicron particles in three different size ranges, and of ozone above the forest canopy. The measured deposition velocities (v_d) of particulate sulfur peaked at about 1 cm s^{-1} in daytime, but dropped to near zero at night, with a long-term average of about 0.6 cm s^{-1}. When scaled with friction velocity, these values of v_d are consistent with similar measurements taken previously over different surfaces. Measurements and analyses indicate that the flux divergence of particulate sulfur should have caused an error no greater than ±0.05 cm s^{-1} in v_d estimates. For very small particles (less than 0.1 μm diameter), measured values of v_d were similar to those for particulate sulfate, but deposition velocities for particles in the accumulation size range decreased as particle size increased, and upward components of fluxes were found in daytime convective conditions. During this study, measurements were also made of sulfur deposition to polycarbonate petri dishes placed in the forest canopy, and to the bucket of a standard wet-dry collector in a forest clearing. These surrogate surface studies produced much smaller values of v_d for sulfate than those derived from eddy correlation, when no scaling as a function of leaf area relative to ground area was applied.

Introduction

Evaluation of dry deposition is a difficult task that requires research to develop dependable methods of measurement and the use of routine observations to make long-term estimates of air-surface exchange. To this end, three Core Research Establishment (CORE) sites for dry deposition research [see Hales et al., 1987] were set up during 1983 and 1984, as a collaborative endeavor of the U.S. Department of Energy, the U.S. Environmental Protection Agency, the U.S. Geological Survey, and the National Oceanic and Atmospheric Administration. The sites are located at Argonne, Illinois, in a grassy field approximately 50 km southwest of Chicago; near State College, Pennsylvania, in a mixed farming and forest region of known high wet acidic deposition; and near Oak Ridge, Tennessee, in a forested research area (Figure 1). Sensors operated at each CORE site record hourly (or more frequent) changes of air chemistry, local meteorological variables, and surface conditions, which must be known to infer deposition rates routinely using existing procedures. In addition, research programs on dry deposition measurement are conducted using a variety of methods and equipment available at each institution carrying out CORE activities, to provide reference dry deposition data for evaluating the results obtained using the more indirect methods (e.g., see Matt et al. [1987] for such an evaluation). As well, each site hosts collaborative multilaboratory field studies and technique comparisons on a rotating basis. One such study is the subject of this paper. The experiment described here was conducted at the Oak Ridge field site in May 1983, during the period of peak leaf-expansion rate. The goal was to investigate flux divergence in the context of the ability of eddy correlation methods to measure dry deposition fluxes of slowly depositing materials, especially particles. The experimental focus was on sulfate aerosol deposition. Ozone fluxes were also measured in order to consider overall canopy exchange characteristics in comparison to past experiments.

Experimental Procedures

The Oak Ridge CORE facility is located in an area selected for research on dry deposition to deciduous forest canopies. The research area is located on the U.S. Department of Energy's Oak Ridge reservation, in eastern Tennessee. Site elevations average around 335 m above sea level. The present report concerns data obtained at the forest meteorology research location, where a scaffolding tower extends to about 18 m above the treetops. The tower is situated on a spur ridge immediately adjacent to the Walker Branch Watershed (operated by Oak Ridge National Laboratory, and as illustrated by Lindberg et al. [1986], for example). The forest cover consists of an uneven-aged mixed-species stand of mainly deciduous trees, predominantly oaks (Quercus alba, Quercus prinus, Quercus velutina, and Quercus falcata) but with some red maple (Acer rubrum) and tulip poplar (Liriodendron tulipifera). The average tree diameter is about 35 cm and average tree height is about 22 m.

[1]Atmospheric Turbulence and Diffusion Division, Air Resources Laboratory, National Oceanic and Atmospheric Administration, Oak Ridge, Tennessee.
[2]Biological, Environmental, and Medical Research Division, Argonne National Laboratory, Argonne, Illinois.
[3]Environmental Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee.
[4]Department of Meteorology, Pennsylvania State University, University Park, Pennsylvania.

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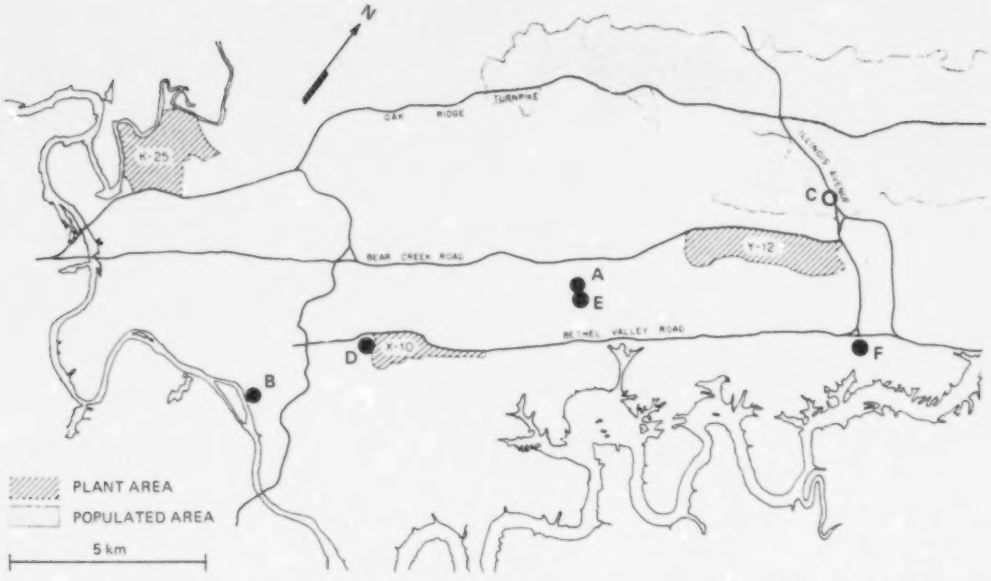

Fig. 1. Details of the area around the Oak Ridge, Tennessee, CORE site (A), showing the satellite site (B), identified for future studies of deposition to a coniferous forest and the current site of the EPRI integrated forest study of deposition, and the location (C) of the NOAA/ARL Atmospheric Turbulence and Diffusion Division. Locations D, E, and F were used to examine local concentration gradients during this intensive study.

Further site details are given elsewhere [see Hutchison et al., 1986].

At regular intervals, pollutant fluxes are measured at the forest meteorology site by eddy correlation, using three-dimensional sonic anemometry and a number of specially modified pollutant sensors. These special instruments include fast-response flame photometers for measuring sulfur dioxide and particulate sulfur, an optical particle sensor, a chemiluminescent ozone sensor, and an infrared carbon dioxide sensor. Because the site is regarded as being micrometeorologically "complex," considerable emphasis is placed on verifying the adequacy of the eddy correlation technique. Hence, sensible and latent heat fluxes are examined in the light of surface energy balance requirements, and friction coefficients derived from values of measured momentum fluxes are compared against estimates based on micrometeorological theory [Verma et al., 1986; Matt et al., 1987].

In general, eddy correlation (covariance) methods are often preferred to alternative micrometeorological methods for measuring turbulent fluxes, because they provide direct evaluations of deposition fluxes across a plane above but near the surface. Gradient techniques also yield fluxes across a plane above the surface, but they require independent evaluation of diffusivities which are frequently difficult to obtain. In complex circumstances, such as those of the field site used in this study, evaluation of appropriate diffusivities is a demanding task that frequently requires measurement of eddy fluxes in any case. Since rapid-response sensors of both ozone and sulfur concentration are available, and since these devices have been tested extensively in previous field studies [e.g., Wesely et al., 1983, 1985; Matt et al., 1987], direct measurement by eddy correlation was selected as the optimal approach for this study.

Standard eddy correlation procedures were employed by both the Argonne and NOAA groups.

TABLE 1. Summary of Instrumentation Employed to Measure Eddy Fluxes During the Oak Ridge Sulfate Deposition Study

Turbulence Sensors	ANL	NOAA/ATDD
Vertical velocity	one-dimensional sonic	three-dimensional sonic
Horizontal velocity	six-cup array	three-dimensional sonic
Temperature	microjunction thermocouple	microbead thermistor
Humidity	Lyman alpha	Lyman alpha
Ozone	ethylene reaction	...
Sulfur dioxide	flame photometer	flame photometer
Particles	electrostatic "charger"	"Climet" optical particle counter

TABLE 2. Specific Modifications Made to Standard Sulfur Flame Photometers for Use in Eddy Correlation Studies.

	ANL	NOAA/ATDD
Model	Meloy 285	Meloy 285 E
Burner block assembly	standard	fast response low volume, with quartz burner tip
Hydrogen flow control	electronic mass flow controller with electrical valve	electronic mass flow controller with thermal valve, standard system bypassed
Sample flow control	critical orifice (standard)	critical orifice (standard, but with pulsation snubber)
Sample acquisition	through a 3-m-long, 1-mm-ID Teflon tube, directly coupled to the standard detector housing	sample extracted from a rapidly aspirated 3-m-long, 8-mm-ID Teflon tube; link to detector is a 20-cm, 1-mm-ID black Teflon tube coupled directly to the burner block fitting
Signal processing	standard electronics replaced by laboratory electrometer	standard linearizing circuitry employed
System response time (exponential)	1.3 s	0.8 s
Sample lag times	5 s	2 s

The procedures employed have been described elsewhere [e.g., Kanemasu et al., 1979; Hicks et al., 1986; Hicks and McMillen, 1988]. Tables 1, 2, and 3 summarize the instrumentation and analysis methods that were used. In the computations of the covariances (fluxes), the time series were shifted to obviate the effects of lag times. Also, the flux estimates were corrected to account for the effects of different response times of the various sensors. After these corrections were made, the uncertainties in the final flux values were estimated to be less than ± 10%.

The flame photometers used for fast-response sensing of sulfur concentration were highly modified commercial instruments (Meloy models 285 and 285 E). In some eddy correlation applications, such sensors are operated with filters to exclude particles from the sampled air stream, so as to provide a measurement of gaseous sulfur, usually sulfur dioxide but possibly with some small level of interference due to other gaseous sulfur compounds. (Experiments conducted at other times have failed to give evidence of a gaseous sulfur component other than SO_2 at the location of this experiment.) In the present case, however, the instruments were operated with an in-line denuder system to remove SO_2 and acidic sulfur gases from the air stream. We assume that the particulate sulfur passing through the denuder tube was entirely sulfate. The configuration of the samplers and the operation of the denuders were designed to provide data representative of particulate sulfate in the accumulation size range, and prohibited efficient sampling of particles larger than one or two micrometers in diameter.

Experience obtained in the operation of highly modified flame photometers such as those considered here suggests that instrument drift and calibration variability are related to factors such as air temperature, humidity, and density, and perhaps concentrations of other trace gases that might be interferents. Drift is often of considerable concern, but the slope of the calibration curves is less variable. Thus, zero-level checks were conducted every few hours in the field, and complete calibrations were carried out every 2 or 3 days. These checks were conducted using methods designed to impose minimal alteration to the normal performance configurations of the instruments.

In the discussion that follows, deposition velocities rather than surface resistances are used to evaluate transfer processes; deposition velocities are a direct computational result that

TABLE 3. Sensor Characteristics and Analytical Program Features

	ANL	NOAA/ATDD
Exponential Response Times (or Distances)		
Vertical velocity	10 cm (sonic) 2 m (propeller)	25 cm (sonic)
Horizontal velocity	60 cm (six-cup)	25 cm (sonic)
Temperature	20 ms	130 ms (thermistor)
Humidity	50 ms	50 ms
Sulfur dioxide	1.3 s	0.8 s
Ozone	0.7 s	...
Covariance Computation		
Computing system	DEC minicomputer	HP-1000L
Digitization rate	20 Hz	10 Hz
Run length	25 min every 30 min	30 min
Data Storage		
Raw data	written directly to magnetic tape (20 Hz)	written directly to magnetic tape (10 Hz)
Processed results	floppy disk, with printer backup	floppy disk, with printer backup
Computation method	Reynolds averaging with coordinate rotation to force average vertical velocity to zero	Reynolds averaging with three-dimensional coordinate rotation

require no inferences about the heights of the aerodynamic surface-displacement planes needed to compute gas-phase resistances above the canopy. These displacement heights are particularly difficult to estimate for tall canopies and are different for various chemical species. For practical purposes, the surface resistances can be estimated as $R_s = (v_d^{-1} - 0.15)$ s cm^{-1} during the daytime and as $R_s = (v_d^{-1} - 1.5)$ s cm^{-1} at night, where the values of 0.15 s cm^{-1} and 1.5 s cm^{-1} are typically within ±50% of the atmospheric component of the overall transfer resistance for individual half-hour estimates.

Results

Eddy Correlation Sulfate Measurements

Figure 2 illustrates the diurnal evolution of sulfate deposition measured on three successive days of the experiment, for which completely independent micrometeorological sensing and analysis systems were used by the NOAA and ANL groups. Following traditional micrometeorological convention, fluxes toward the surface (i.e., deposition) are shown as negative values. In fact, no positive (upward) fluxes of sulfur were measured at any stage by the NOAA equipment, and only infrequently by the ANL sensor. The standard error bars associated with the ANL data in Figure 2 indicate that the ANL upward fluxes were probably not significantly different from zero. The NOAA results shown in Figure 2 were obtained at a height of 15 m above the top of the canopy; the ANL sulfur sensor and eddy correlation instruments were mounted 9 m lower, yet were generally in agreement with the NOAA results. Considerable half-hour to half-hour scatter was evident in the ANL data because of sensor "noise," similar to that described by Wesely and Hart [1985] and considerably greater during this experiment than the noise in the NOAA sulfur sensor.

Inspection of Figure 2 reveals the strong diurnal cycle that is now an expected feature of such air-surface exchange. In daytime, deposition rates peaked in the range of 0.05 to 0.1 μg m^{-2} s^{-1} of sulfate. During the entire period,

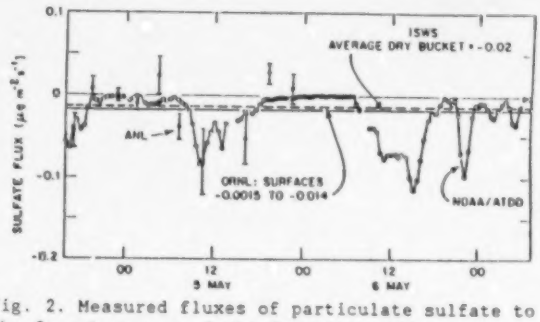

Fig. 2. Measured fluxes of particulate sulfate to the forest canopy of the Oak Ridge CORE site. Negative fluxes indicate downward transfer, thus surface deposition. The open circles represent individual half-hour values, the solid dots and standard error bars are computed for 3 h of data. The ORNL "surface" data were collected using petri dishes. Both these and the ISWS bracket samples represent estimates averaged over at least 1 week.

half-hour averaged concentrations varied from 2 to 15 μg m^{-3}, based both on measurements by the flame photometric sulfate sensors and an air filterpack sampler. Sulfate deposition velocities corresponding to the times shown in Figure 2 varied from near zero in light winds at night to over 1.0 cm s^{-1} during the daytime. The overall average value for the period was approximately 0.6 cm s^{-1}.

On the whole, the sulfate aerosol eddy correlation results did not diverge significantly from the relationships suggested by Wesely et al. [1985]. While these limited data produced rather large values of v_d, normalization by division by u_* produces estimates of v_d/u_* equal to approximately 0.02 for moderately unstable conditions and 0.001 for a stably stratified atmosphere. The canopy was apparently quite efficient in removing particulate material, despite the fact that the leaf area was only about 50% of that for the forest canopy in midsummer.

Surrogate Surface and Bucket Measurements

Measurements of sulfate deposition to polycarbonate petri dishes distributed throughout the canopy at heights of 20 to 25 m above the ground, and to the dry bucket of a standard wet-dry collector 1 m above the ground in a clearing in the forest were made by personnel of Oak Ridge National Laboratory (ORNL), at locations from 20 to 500 m from the tower used for the micrometeorological studies. The averaging times involved in these collection surface measurements were much larger than those of the micrometeorological measurements: days versus hours. Thus, a direct comparison of simultaneous results of the different methods can be accomplished only with considerable averaging of the micrometeorological data.

As a first guess, we might expect that the deposition to an inert (surrogate) surface should be scaled approximately according to the amount of leaf area in the canopy in order to compare results with eddy fluxes, since micrometeorological techniques apply to the canopy as a whole. The validity of direct comparisons, however, is limited by several factors. For example, surrogate surfaces collect particles larger than those detected by the eddy correlation sulfur sensing system, which is effectively restricted to detecting particles less than 2 μm diameter. Both the number- and mass-median diameter of particles deposited to inert surfaces at this site exceeded 2 μm [Coe and Lindberg, 1987]. Also, the collection efficiencies of submicron particles for leaves may be different from the inert surfaces. Many of these factors and the methods of deploying and analyzing the petri dishes have been discussed by Lindberg and Lovett [1985].

Values of v_d for deposition to individual petri dishes (the ORNL "surfaces" of Figure 2) averaged about 0.05 cm s^{-1} during the week before the period illustrated in Figure 2, and about 0.15 cm s^{-1} during the period immediately following it. (Unfortunately, samples were not collected during May 5 and 6.) For purposes of comparison to the eddy flux values shown in Figure 2, an average value of about 0.1 cm s^{-1} appears an appropriate approximation of the surrogate-surface deposition result. This value of deposition velocity is about a factor of 5 smaller than the eddy correlation result, a factor within ±50% of the ratio of canopy leaf area (which was not measured precisely) to underlying ground area during the experiment. During summer, when the canopy is fully developed, throughfall analyses suggest that the particle sulfate dry deposition to the forest canopy is about 2 or 3 times the flux to these surrogate surfaces [Lindberg et at., 1986].

In comparison, results obtained at the dry deposition intercomparison experiment in 1981 and 1982 indicate that petri dishes exposed 15 cm over short grass collected more sulfate than found by eddy correlation [Davidson et al., 1985; Dolske and Gatz, 1985; Wesely et al., 1985; Hicks, 1986]. In addition to the factors already mentioned that might help explain some of these differences, the level of turbulence to which the petri dishes were exposed in the forest canopy was undoubtedly considerably lower than when placed above a short grass surface. Hence, the scaling factor of 5 for deposition velocity over the forest may depend on many factors, and probably is not always simply related to the amount of leaf area exposed in the canopy. In any case, these and other studies [e.g., Bytnerowicz et al., 1987] indicate that scaling with leaf area seems most valid when the petri dishes are placed within the canopy rather than above it.

As shown in Figure 2, operation of the petri dishes yielded a range of sulfate fluxes in the 3- to 4-day periods before and after May 5 and 6. It should be noted that the lower value was the lowest sulfate flux ever measured at this site and is not representative. The mean deposition rate to petri plates during the summers of 1981-1983 (0.012 μg/$m^{-2}s^{-1}$, N=110) was similar to the higher value in this range. Also illustrated are the results obtained using dry-bucket collections, derived using the procedures of the National Atmospheric Deposition Program (NADP). One-week sampling was employed, with subsequent analysis by the central analytical laboratory of the Illinois State Water Survey (ISWS). The bucket sample yielded an average sulfate

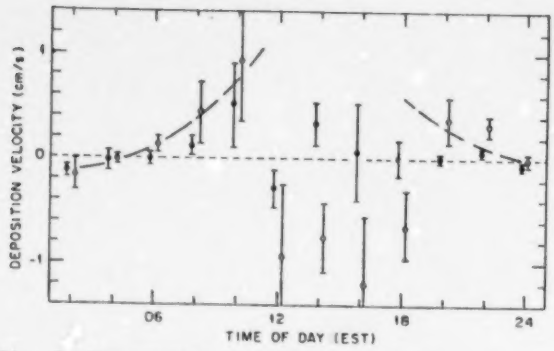

Fig. 3. The average diurnal cycle of apparent deposition velocity for small particles with diameters of 0.5 to 0.7 μm (open circles) and 0.7 to 1.2 μm (solid circles). The points and corresponding standard error bars were computed from averaging original half-hour determinations.

deposition rate ~2.5 times greater than the average obtained from the petri dishes.

Comparing the mean surrogate surface results is not straightforward because of differences in their height of deployment above the ground and exposure periods. However, the trend in measured fluxes is similar to other experiments. For example, buckets also collected twice the sulfate deposition amounts collected by petri dishes at the dry deposition intercomparison experiment [Dolske and Gatz, 1985; Feely et al., 1985]. Dasch [1985] has shown that the properties of the substances used to construct the surrogate surfaces and their geometries (see also Hicks [1986] can also influence the amount of sulfate accumulated.

Particle Deposition Velocities

Figure 3 shows the average diurnal cycle of particle deposition velocities, obtained during several days of the experiment. These particle fluxes were measured by eddy correlation, with an optical particle counter arranged to provide two independent fast response outputs corresponding to particle number density in the size ranges of 0.5 to 0.7 and 0.7 to 1.2 μm diameter. The complicated behavior evident in the diagram and the scatter associated with the determinations (standard error bars are indicated) contrast with the well-behaved time sequence evident for sulfate deposition in Figure 2. Close inspection of Figure 3 reveals some support for the theoretical prediction that larger particles will be deposited with larger deposition velocities, but this feature is only apparent during limited periods. During the central part of the day, fluxes of particles in both size ranges tended to be directed upwards from the canopy (negative apparent deposition velocities), suggesting a dominant role of particle production within the canopy or emission from it. Similar behavior has been observed previously, and indeed seems to be a characteristic of such studies. Some of these situations have been reviewed by Lee and Wesely [1988], who concluded that such upward fluxes for particles larger than about 0.2 μm in diameter are probably not associated with the growth and shrinkage of particles caused by transport through vertical gradients of humidity. Their conclusion is not contradicted by the data shown in Figure 3 because the upward fluxes occur most strongly during the afternoon when relative humidities were lower than during other portions of the day. Other causes, such as particle resuspension, are more likely. Evidence for in-canopy sources of coarse particle sulfate at this site has been discussed by Lindberg and Lovett [1985].

Figure 4 reveals a far less complicated picture for particles in the 0.05 to 0.10 μm diameter range size, as measured by the ANL instrumentation using an electrostatic "charger" system [Wesely et al., 1977]. The data are presented as an average diurnal cycle, as in Figure 3. The values plotted have been derived for a 10-day period encompassing the period of more intensive study discussed above. Overall, these small-particle data are consistent with findings presented previously for a leafless deciduous canopy [Wesely et al., 1983]. No significant case of upwardly directed net exchange was detected, which supports the contention that vertical humidity gradients had no significant effect on particle fluxes. Also, since the small particles would probably be more strongly affected by gas-to-particle conversion of surface-emitted hydrocarbons than would be the larger particles addressed in Figure 3, it seems reasonable to rule out gas-to-particle conversion as the major source of the upward fluxes of those larger particles.

Ozone Exchange

The ANL team made measurements of ozone fluxes during these intensive experiments. The results yielded deposition velocities similar to those derived earlier for a different deciduous forest in wintertime [Wesely et al., 1983]. As shown in Figure 5, deposition velocities displayed the now-familiar tendency to be small at night, less than 0.1 cm s^{-1} in this case. Greater mixing and thus greater penetration of O_3 to destruction sites deep in the canopy are revealed by a dependence of v_d on u_*. During the daytime,

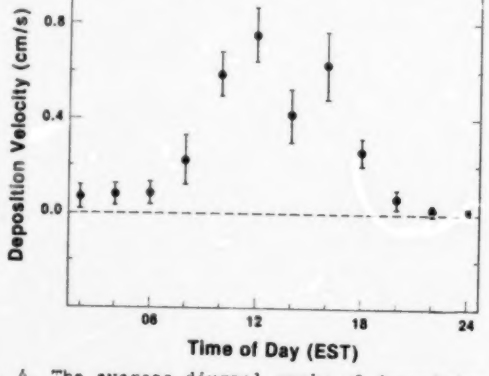

Fig. 4. The average diurnal cycle of deposition velocity measured for small particles approximately 0.05 to 0.1 μm in diameter, plotted as in Figure 3.

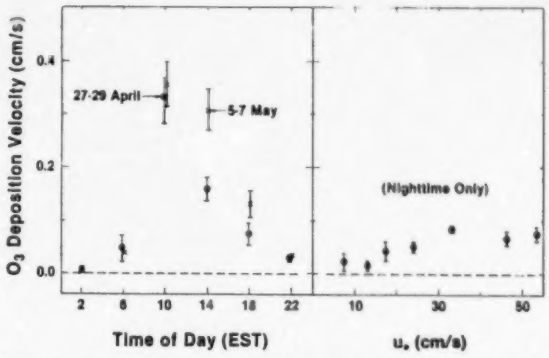

Fig. 5. Deposition velocities for ozone, averaged to display the average diurnal cycle (left-hand side) and the dependence on friction velocity at night (right-hand side).

deposition velocities are less than 0.4 cm s^{-1}, with slightly greater midafternoon values in the later part of the experimental period, when the canopy was more leafy. Maximum deposition velocities between 0.5 and 1.0 cm s^{-1} are expected in summer when removal by transport through plant leaf stomata is efficient. Since daytime O_3 deposition velocities over a practically inert, deep canopy of deciduous forest during the winter were similar to the values reported here, it seems that little of the O_3 removal detected in the present study was via plant leaf stomata.

Flux Divergence

The issue of interest is whether a measurement of the appropriate deposition velocity at some height above the surface is an accurate determination of the value relevant for computation of dry deposition at the surface itself. This question is over and above considerations of sampling statistics and noise, which are addressed elsewhere [Fairall, 1984; Wesely and Hart, 1985; Lenschow and Kristensen, 1985].

Measurements of flux divergence involving eddy correlation focused mostly on sulfur deposition. The results indicated in Figure 2 were obtained using two independent sets of sulfur flux measuring apparatus erected above the canopy, one set operated by ANL, the other by NOAA. Although the sensors were vertically separated by nine meters, it appears that no statistically significant differences were detected. Despite the apparent agreement of the eddy flux measurements, the absence of significant flux divergence has not been proven, because side-by-side operation of the sensors at the same height was not able to demonstrate conclusively that there were no systematic differences in the fluxes measured by ANL and NOAA.

At the same time as flux divergences were being investigated directly, a mobile set of air chemistry sensors from the Pennsylvania State University (PSU) were used by PSU researchers to search for evidence of local concentration gradients along the direction of the mean wind. As will be discussed later, horizontal gradients can be related to vertical flux divergerences. Measurements were made between locations approximately 5 km apart, identified in Figure 1. For sulfur dioxide, the average horizontal concentration gradient measured when the daytime data for Figures 2-5 were collected was 0.8% km^{-1}, with a standard error of 1.1% km^{-1}. For small particles (measured as concentration nuclei with a CCN counter), the average gradient was 1.0 ± 0.7% km^{-1}. Thus, it appears that the gradients were very small, and usually not statistically different from zero.

Although measurement difficulties prohibited the direct determination of the horizontal (longitudinal) gradient of sulfate aerosol, we do not suspect that the behavior of sulfate differed from that reported above for sulfur dioxide and submicron particles in general.

Expansion of the relevant relationships, as reviewed by Wesely et al. [1985], shows that the important terms are associated with the following: time stationarity, $\partial C/\partial t$; horizontal advection, $u(\partial C/\partial x)$; and the change of flux with height, $\partial F/\partial z$. The first two terms can be considered as separate contributions to a total error in the determination of the deposition velocity $v_d = -F/C$; this error results from the fact that measurements are made not at the surface itself but at some height above it. Here, terminology follows usual meteorological convention: z is the height above the appropriate zero plane, F is the flux (positive upward), C is concentration at height z, t is time, u is the wind speed, and x is distance along the wind vector. It is convenient to consider these factors in terms of the proportional rates of change of concentration with time [$\delta_t C \equiv C^{-1}(\partial C/\partial t)$] and with longitudinal distance [$\delta_x C \equiv C^{-1}(\partial C/\partial x)$].

A standard micrometeorological guideline indicates that effects of local changes with time can be neglected provided concentrations do not change by more than 10% h^{-1}. If measurements of fluxes were made at a height of 9 m above the zero plane displacement height in conditions with $\delta_t C = 10\%\ h^{-1}$, then the resulting error in the evaluation of the deposition velocity would amount to about 0.03 cm s^{-1}. This error scales in a manner that is obvious from inspection of the appropriate term, with a proportionality that is approximately linear with height of measurement. This particular term does not normally impose great difficulties for experimenters, because it can be evaluated from the single-point data obtained in the normal course of an experiment and because computation of the appropriate corrections is relatively easy. It is usually the advective term which is difficult to handle. In the present case, the averages and standard errors found for the gaseous and aerosol gradients suggest that the horizontal advection error term was probably less than $\delta_x C = 1\%\ km^{-1}$. In the conditions of the present study, with about 2 m s^{-1} wind speed and with the height of measurement being nine meters, simple calculations show that the error involved with the measurement of v_d was therefore probably less than 0.02 cm s^{-1}.

The level of uncertainty associated with measurements of v_d by micrometeorological methods applied about nine meters above the canopy zero plane, and due to causes related to local flux divergence, is thus on the order of 0.05 cm s^{-1}. Inspection of the individual contributions shows that the "error" increases as the height of

measurement increases. It is of passing interest that this level of uncertainty is similar in magnitude to the size of corrections normally required to account for effects of density fluctuations (incorporating Stefan flow) as described by Webb et al. [1980].

Conclusions

The air-surface exchange of particles and gases was measured successfully over a mixed-species deciduous forest during springtime near Oak Ridge, Tennessee. Eddy correlation was used to measure the vertical fluxes several meters above the forest canopy, for particles in three size ranges, submicron particulate sulfur (sulfate), and ozone. Other micrometeorological measurements, not reported here, included the exchange of heat, moisture, and momentum. Inert surrogate surfaces were also used nearby to measure coarse particle deposition. The fluxes were measured over several diurnal cycles, which were characterized by generally dry conditions, convective conditions during midday, and extremely limited gas exchange via leaf stomata because the leaves were immature, though emerging rapidly through a stage of about 50% of maximum leaf area.

Changes of particulate sulfur fluxes with height, as measured by two eddy correlation systems, appeared negligible. Measurements of horizontal gradients of particles and gases upwind of the site supported this finding. Provided that standard micrometecrological constraints on site uniformity and time stationarity are adhered to, eddy correlation (and other micrometeorological methods for measuring fluxes through air above the surface) in general appear capable of resolving deposition velocities to about 0.05 cm s^{-1}. This limit of resolution is appropriate for the present study and does not interfere with its conclusions.

This study found that the flux of submicron particulate sulfate was unidirectional, toward the surface. Likewise, it appeared that the deciduous forest was always a sink for very small particles (diameter less than 0.1 μm); the surface apparently was not sufficiently wet to cause upward fluxes as a result of interactions between particles and water vapor. On the other hand, this study has demonstrated that the exchange of particles in the so-called accumulation size range (of particles resulting from nucleation, condensation, and coagulation) is more complicated; in general, the canopy must be considered as both a source and a sink, with probably strong diurnal variations in the strengths of both. Specifically, the upward components of fluxes of particles in the size ranges of 0.5 to 0.7 μm and 0.7 to 1.2 μm in diameter appeared to be strongest during the warmest and usually the most convective daylight hours. This upward flux was most evident for the 0.5-0.7 μm particles.

For those occasions in which particle fluxes appeared most unaffected by variable surface sources, a particle-size dependence of deposition velocity was found, as is generally predicted by theory. At the same time, the deposition velocity for submicron particulate sulfate in terms of friction velocity and atmospheric stability appeared to conform to parameterizations previously derived, which were based on eddy correlation methods similar to those used in this study.

If particle size is considered as the sole basis for classification of particles, then it is not possible to distinguish between the particles emitted from a canopy and those being deposited to it. The questions of major interest concerning the validity of alternative numerical models of small particle deposition will probably remain unanswered until some method is developed to measure particle loading as a function of chemical species concurrently with particle size.

The influence of leaf area on particle deposition continues to be explored. It appears that the leaf area index (LAI, total leaf area per unit of horizontal area at the ground) might be a reasonable scaling factor, within a factor of about two, to relate sulfate measured by petri dishes in the canopy to overall sulfate deposition in the canopy. Further studies, in which LAI and type of vegetation vary extensively, are needed to investigate the behavior of such a scaling factor. Also, the roles of deposition of large particles, gas-to-particle conversion on the inert surfaces, and weighting of results from petri dishes by horizontal strata in the canopy have not been addressed here. These factors are currently under investigation in longer-term studies utilizing methods similar to those described here, in addition to throughfall studies at this and other sites.

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D. R. Cook, R. L. Hart, and M. L. Wesely, Bldg. 203, BEM/CER, Argonne National Laboratory, Argonne, IL 60439.

R. D. de Pena and D. W. Thomson, Department of Meteorology, Pennsylvania State University, University Park, PA 16802.

B. B. Hicks, D. R. Matt, R. T. McMillen, and J. D. Womack, Atmospheric Turbulence and Diffusion Division, NOAA/ARL, P. O. Box 2456, Oak Ridge, TN 37831.

S. E. Lindberg, Environmental Sciences Division, Oak Ridge National Laboratory, P. O. Box 2008, Oak Ridge, TN 37831-6038.

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